

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-143202  
(43)Date of publication of application : 23.05.2000

---

(51)Int.Cl. C01B 3/06

---

(21)Application number : 10-356846 (71)Applicant : CENTER FOR COAL UTILIZATION

JAPAN  
AGENCY OF IND SCIENCE &  
TECHNOL  
HATANO HIROYUKI  
SUZUKI ZENZO

(22)Date of filing : 11.11.1998 (72)Inventor : HAYASHI SEKIEI  
HATANO HIROYUKI  
SUZUKI ZENZO

---

(54) PRODUCTION OF HYDROGEN BY THERMOCHEMICAL DECOMPOSITION

(57)Abstract:

**PROBLEM TO BE SOLVED:** To high efficiently and selectively take out hydrogen as thermodynamic chemical equilibrium is kept by allowing a material containing carbon such as an organic material to react with supercritical water in the presence of a material absorbing carbon dioxide in the quantity enough to absorb all generated carbon dioxide.

**SOLUTION:** A material containing carbon such as coal, petroleum, plastic, biomass is reacted with supercritical water under  $\geq 220$  atm at  $\geq 600^\circ$  C, preferably under 250–600 atm at 650–800° C. As a result, the oxidation is performed with dissolved oxygen without adding an oxidizing agent. The equilibrium reaction of a gas produced by the reaction of the organic material with supercritical water is expressed by a formula,  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ . The reaction proceeds by taking out  $\text{CO}_2$  as a carbonate in the presence of the material absorbing  $\text{CO}_2$  such as  $\text{CaO}$ ,  $\text{MgO}$  and an oxidizing acid. In such a case, the presence of the sufficient quantity of a material for taking out sulfur, halogen or the like as a water soluble salt, such as  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{KOH}$ ,  $\text{K}_2\text{CO}_3$ , is preferable.

---

LEGAL STATUS

[Date of request for examination] 11.11.1998

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 2979149

[Date of registration] 17.09.1999

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

## \* NOTICES \*

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## CLAIMS

---

## (57) [Claim(s)]

[Claim 1] The manufacture approach of hydrogen of performing thermochemical decomposition, without making the matter containing carbon reacting with supercritical water, being the approach of returning supercritical water and making hydrogen generating, and making it existing in the amount system of reaction which can absorb all the carbon dioxides that generated the carbon-dioxide absorbing material at least, and adding a parenchyma top oxidizer on conditions with a 220 or more atmospheric-pressures temperature [ of pressures ] of 600 degrees C or more.

[Claim 2] The manufacture approach of the hydrogen which supplied the matter and carbon-dioxide absorbing material containing carbon to the system of reaction, and was indicated by claim 1 which takes out hydrogen and a carbonate from the system of reaction.

[Claim 3] The manufacture approach of the hydrogen indicated by claim 1 or claim 2 which decomposes a carbonate thermally, changes into a carbon-dioxide absorbing material, and is again returned to the system of reaction.

[Claim 4] The manufacture approach of the hydrogen indicated by one of either claim 1 using CaO, MgO, or an iron oxide as matter which absorbs a carbon dioxide thru/or the claims 3.

[Claim 5] The manufacture approach of hydrogen that the matter containing carbon was indicated by one one of claims 1 thru/or claims 4 which is coal, petroleum, plastics, biomass, any one \*\*, or two or more.

[Claim 6] The manufacture approach of the hydrogen indicated by one of either claim 1 whose reaction temperature is 650 degrees C – 800 degrees C thru/or the claims 5.

[Claim 7] The manufacture approach of the hydrogen indicated by one of either claim 1 made to exist in the amount system of reaction which absorbs all of sulfur, a halogen, and the sulfur which generated at least the matter which forms a water-soluble salt and a halogen with a carbon-dioxide absorbing material thru/or the claims 6.

[Claim 8] as the matter which forms sulfur, a halogen, and a water-soluble salt -- NaOH and Na<sub>2</sub> -- the manufacture approach of the hydrogen indicated by one of either claim 1 using one sort of the compound chosen from the group which consists of CO<sub>3</sub>, KOH, and K<sub>2</sub>CO<sub>3</sub>, or two sorts or more thru/or the claims 7.

---

[Translation done.]

## \* NOTICES \*

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] The hydrogen manufacture approach of pyrolyzing the organic substance, such as coal and petroleum, with elevated-temperature high pressure, and manufacturing hydrogen gas, the manufacture approach of the hydrogen from water gas, the manufacture approach of the hydrogen which electrolyzes water, etc. are learned from the former. The place by which this invention belongs to the technical field which manufactures such hydrogen, and it is characterized [ the ] uses the heat generated in case the carbon in the organic substance is oxidized, and is related with the approach of disassembling supercritical water thermochemically and manufacturing hydrogen alternatively.

[0002]

[Description of the Prior Art] Although there are some processes which disassemble and gasify the organic substance, such as coal, petroleum, plastics, and biomass, most oxidative degradation methods are used. Since catabolic rate is high, the oxidative degradation method for using supercritical water also in an oxidative degradation method is used well recently. The oxidative degradation method of the organic substance for having used conventional supercritical water for drawing 1 is shown. It is mixed with water, and after the organic substance is fed with a pump 2 by the reactor 1 with which water will be in a supercritical condition and secures fixed time amount reaction time within a reactor with a temperature of about 400 degrees C, it is divided into the gas oxidative degradation product which cooled and decompressed and was generated with the condensator 3, water, and solid-state residue. At this time, when air or oxygen is separately supplied to a reactor 3 as an oxidizer and the heat to generate runs short, a supercritical condition is maintained by applying heat from the exterior. In such an operating condition, the nitrogen gas with which the gas oxidative degradation product was generated from the nitrogen content in a carbon dioxide and the organic substance occupies most. In the case of the gas pyrolysis and many which use a carbon monoxide, a carbon dioxide, a low-grade hydrocarbon, hydrogen, and nitrogen as a principal component in this case, a liquefied product is obtained although there is also the decomposing method only the heat from the outside performs a pyrolysis at the temperature of 400-600 degrees C supercritical underwater, without adding an oxidizer. The yield of hydrogen is low, although the yield of gas becomes high so that it pyrolyzes at an elevated temperature. Returning supercritical water and taking out hydrogen using the carbon in the organic substance, although research was variously done about disassembling the organic substance by supercritical underwater and conventionally taking out the gas of the organic substance origin was not noted, and it was not considered. this invention person used to find out that what is necessary is just to combine the supercritical water and the carbon-dioxide absorbing material of specific conditions, without adding a parenchyma top oxidizer, as a result of narrowing [ a lifting and ] down a target to the ability of supercritical water to be returned efficiently and studying thermochemical disassembly of water wholeheartedly how from such a viewpoint.

[0003]

[Problem(s) to be Solved by the Invention] When disassembling the organic substance, without

adding an oxidizer with the water of a supercritical condition, in the reaction temperature of about 400 degrees C, the gas which the pyrolysis of the organic substance is not carried out completely, but uses a carbon monoxide, a carbon dioxide, hydrogen, nitrogen, a low-grade hydrocarbon, etc. as a principal component, and a liquefied product are generated. There are very few rates of the hydrogen generated at this time. If reaction temperature is raised at 650 more degrees C, a liquefied product will disappear and the organic substance will be gasified completely. However, the presentation of generation gas uses a carbon monoxide, a carbon dioxide, and hydrogen as a principal component, the presentation stops at the thermodynamical equilibrium value determined with reaction temperature and reaction pressure, and the rate of hydrogen gas becomes about 30%. This invention succeeds in raising the rate of the hydrogen in generation gas by leaps and bounds, maintaining this thermodynamic chemical equilibrium using the supercritical water and the generating gas absorption matter of specific conditions. Furthermore, it found that it is finally also recoverable as a water-soluble salt, without catching sulfur and a halogen with a reactor and making them shift into the gas to generate. In this invention, the semantics of not adding a parenchyma top oxidizer also means that it is not necessary to remove specially the air which faces loading a reactor with others, a sample, or a raw material, and is included in a sample thru/or a raw material. [ semantics / that it is not necessary to add an oxidizer ] Since this does not need to send in air with high pressure, it also becomes reduction of compression power and leads also to the advantage which does not require the operating cost of the whole equipment.

[0004]

[Means for Solving the Problem] In the 650-degree C pyrolysis of the organic substance supercritical underwater [ above-mentioned ], the rate of the hydrogen in gas does not become high, because the carbon monoxide in the gas formed at the reaction of the organic substance and the water of a supercritical condition, a steam, a carbon dioxide, and hydrogen are in chemical equilibrium. Static reaction  $CO + H_2 O \rightleftharpoons CO_2 + H_2 \dots (1)$

It is described by \*\*\*\*\*. The operation which reacts with a carbon dioxide on condition that the temperature of a reactor and a pressure here, and is fixed as a solid-state is carried out, and if the matter (carbon-dioxide absorbing material) which does not affect this chemical equilibrium relation at all is made to live together at a reaction place superfluously beforehand in itself, the amount of the carbon dioxide in gas will decrease by the reaction with this matter.

[0005] In order to maintain the above-mentioned chemical equilibrium relation to the amount of this carbon dioxide that decreased in number, a reaction advances in the direction which generates  $CO_2$  and  $H_2$  by the reaction of  $CO$  and  $H_2O$  inevitably. Produced  $CO_2$  reacts with a carbon-dioxide absorbent, and is removed from gas. As a result, finally, it becomes chemical equilibrium into gas in the form where a carbon monoxide, a carbon dioxide, and a lot of steams and hydrogen of \*\*\* small quantity exist. Gas and a solid-state (mixture of the solid matter which absorbed the ash content, the unreacted diacid carbonizing absorbent, and carbon dioxide in the organic substance, and was produced) become possible [ dissociating, since a steam returns to water by cooling ]. It becomes possible to manufacture the gas which uses hydrogen as a principal component from the organic substance as a result. It is a reaction formula if a carbon-dioxide absorbent is now set to X.  $C + 2H_2 O + X \rightleftharpoons (XCO_2) + 2H_2 \dots (2)$

It can come out and describe. The hydrogen gas to generate can make water the origin, it can be shown that the above-mentioned generalization reaction formula manufactures hydrogen alternatively from the carbon and water in the organic substance, and this can be regarded as the thermochemical decomposition reaction of water.

[0006] Although such [ naturally ] heat can also be used since heat of reaction is emitted when the carbon-dioxide absorbing material, for example,  $CaO$  etc., added to the system of reaction besides the heat of combustion generated in case the carbon which the organic substance holds as a heat source which drives a reaction is oxidized reacts with water and it is set to calcium  $(OH)_2$ , when it runs short, (2) types can be advanced by applying heat from the exterior. When Matter X is used as a carbon-dioxide absorbent  $X + CO_2 \rightleftharpoons XCO_2 \dots (3)$ ,

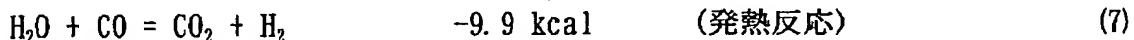
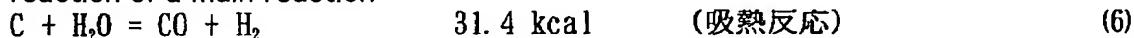
In order to produce \*\*\*\*\*, it must be beyond the temperature that becomes settled thermodynamically. Therefore, the temperature of the system of reaction of this invention turns

into beyond the temperature that the above-mentioned reaction formula (3) produces inevitably, as a carbon-dioxide absorbent, metallic oxides, such as CaO, MgO, and an iron oxide (FeO, Fe 2O3, Fe3O4), and the hydroxide (calcium -- (OH) -- two -- Mg -- (OH) -- two -- Fe -- (OH) -- two -- Fe -- (OH) -- three -- a grade) of a metal of the same kind are typical. Since it is economical, CaO and calcium (OH)2 are the matter recommended most. Moreover, although not mentioned as an example, MgO and Mg (OH)2, FeO, Fe 2O3, and Fe3O4 are checking the effective thing. A hydroxide is dehydration at hot conditions. calcium (OH)2=CaO+H2O ..... (4)

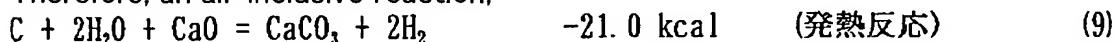
$$\text{Mg(OH)}_2 \rightleftharpoons \text{MgO} + \text{H}_2\text{O} \quad \dots \quad (5)$$

The case where a metallic oxide of the same kind is added from the beginning by that of \*\*\*\*\*  
 and a reaction place become equal. The sulfur content in the organic substance generates [ in water ] a poorly soluble sulfate in this case and is not desirable, although it reacts with X and is fixed as a sulfate in the above-mentioned reaction process. In order to prevent this, H<sub>2</sub>S once produced in gasification apart from X and the matter Y which is easy to react are added, and the matter water-soluble at the reaction of Y and H<sub>2</sub>S is made to form.

[0007] Consequently, since the sulfur in the organic substance serves as water solubility, the ash content in the carbon-dioxide absorbing material and the unreacted carbon-dioxide absorbing material after a reaction, and the organic substance etc. is separable from other solid-states. It is fixable as a water-soluble salt similarly about a halogen. as Matter Y -- NaOH and Na2 -- there are  $\text{CO}_3$ , KOH, and  $\text{K}_2\text{CO}_3$ . Moreover, in many cases, since Matter Y acts as a catalyst which promotes the reaction of the organic substance and the water of a supercritical condition, it is convenient. Moreover, although the case where  $\text{Na}_2\text{CO}_3$  was used as an example was shown, it is checking that NaOH, KOH, and  $\text{K}_2\text{CO}_3$  also carry out the same operation. A thermodynamic examination is required for ascertaining of whether a reaction advances. Heat of reaction of a main reaction



Therefore, an all-inclusive reaction,



It is net exothermic reaction at least, and has expected a next door and going on spontaneously thermodynamically.

〔0008〕

[Embodiment of the Invention] The gestalt of operation of this invention is as follows.

(1) The manufacture approach of hydrogen of performing thermochemical decomposition, without making the matter containing carbon reacting with supercritical water, being the approach of returning supercritical water and making hydrogen generating, and making it existing in the amount system of reaction which can absorb all the carbon dioxides that generated the carbon-dioxide absorbing material at least, and adding a parenchyma top oxidizer on conditions with a 220 or more atmospheric-pressures temperature [ of pressures ] of 600 degrees C or more.

(2) The manufacture approach of the hydrogen which supplied the matter and carbon-dioxide absorbing material containing carbon to the system of reaction, and was generated, and the hydrogen was used in the light hydrocarbon synthesis reaction.

hydrogen indicated by claim 1 which takes out a carbonate from the system of reaction.  
(3) The manufacture approach of the hydrogen indicated by claim 1 or claim 2 which decomposes a carbonate thermally, changes into a carbon-dioxide absorbing material, and is again returned to the system of reaction.

(4) The manufacture approach of the hydrogen indicated by one of either claim 1 using CaO, MgO, or an iron oxide (FeO, Fe 2O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>) as matter which absorbs a carbon dioxide thru/or the claims 3

(5) The manufacture approach of hydrogen that the matter containing carbon was indicated by

one one of claims 1 thru/or claims 4 which is coal, petroleum, plastics, biomass, any one \*\*, or two or more.

(6) The manufacture approach of the hydrogen indicated by one of either claim 1 whose reaction temperature is 650 degrees C – 800 degrees C thru/or the claims 5.

(7) The manufacture approach of the hydrogen indicated by one of either claim 1 whose pressures are 250 thru/or 600 atmospheric pressures thru/or the claims 6.

(8) The manufacture approach of the hydrogen indicated by one of either claim 1 made to exist in the amount system of reaction which absorbs all of sulfur, a halogen, and the sulfur which generated at least the matter which forms a water-soluble salt and a halogen with a carbon-dioxide absorbing material thru/or the claims 6.

(9) as the matter which forms sulfur, a halogen, and a water-soluble salt -- NaOH and Na2 -- the manufacture approach of the hydrogen indicated by one of either claim 1 using one sort of the compound chosen from the group which consists of CO3, KOH, and K2CO3, or two sorts or more thru/or the claims 7.

[0009]

[Explanation of concrete implementation of invention] It carried out using the micro autoclave 5 with an outer diameter of 30mm which has the capillary tube 7 shown in drawing 2. The pressure in a micro autoclave was changed by adjusting the volume and heating temperature of the amount of pure water with which it is filled up in early stages. Reaction pressure was calculated with the equation of state of water.

[0010]

[Equation 1]

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

p: pressure R:gas constant T:absolute-temperature Vm: -- the volume a which water occupies, and b: -- a constant [0011]

[Example 1] 4.0 cc of pure water of the amount of conventions is mixed with 0.1g (76% of carbon contents) of Pacific Ocean charcoal and 0.6g of calcium(OH)2 powder of the superfluous equivalent ground in the reaction container 6, and it poured into the reaction container 6 with a bore of 12mm with the syringe, heat tracing of it was carried out with the electric furnace, and it was made to react for 20 minutes with 1000 atmospheric pressures of 650 degrees C from the capillary tube 7 with an aperture of 1.6mm. While cooling after the reaction, collecting the gas which occurred in the sampling bag and measuring generating capacity, the presentation was measured by the gas chromatograph. The solid-state and liquid inside a reactor analyzed by collecting.

[0012]

[Example 2] 0.1g of sodium carbonates was added to the sample, and also the same actuation was repeated on the same conditions as an example 1.

[Example 3] The pressure was changed to 300 atmospheric pressures, having used as one cc the amount of the pure water which fills up 0.03g with the Pacific Ocean charcoal, and is filled up with 0.2g and Na2CO3 for calcium (OH)2 0.03g and the first stage, and also the same actuation as an example 1 was repeated.

[Example 4] The pressure was changed to 250 atmospheric pressures, having used as 0.55 cc the amount of the pure water which fills up 0.025 with the Pacific Ocean charcoal and is filled up with 0.15g and Na2CO3 for calcium (OH)2 0.025g and the first stage, and also the same actuation as an example 1 was repeated. For the comparison, the sample which ground only coal was made and others repeated the same actuation as an example 1. Drawing 3 shows the result. The amount of the gas obtained even if it carries out pyrolysis processing by 1000 atmospheric pressures and 650-degree C supercritical underwater does not pass [ g ] only over coal and water in 0.7l. /, and the rate of hydrogen is also as low as 48%. The rate of hydrogen becomes 78% while generation capacity will increase by 2.5 times, if calcium (OH)2 which is a diacid carbonizing absorbent is added to this system of reaction. Furthermore, if Na2CO3 is added, generation capacity will increase further. This drawing shows that Na2CO3 has a function as a

catalyst which raises the reaction rate of a reaction formula (2). Of course, sulfur is caught by addition of  $\text{Na}_2\text{CO}_3$  as water-soluble salts. Although the capacity which will be generated if reaction pressure is lowered decreases, the rate of the hydrogen in gas is still high, and is only judged that it is that the reaction rate only fell. Drawing 3 is drawing having shown the concrete result, and is also the proof which proves work of the additive in this invention to coincidence. If reservation of a heat source is possible as mentioned above, since two-mol hydrogen is manufactured from one mol of carbon, in the case of coal (76% of carbon contents), the hydrogen of  $2.83\text{Nm}^3/\text{kg}$  can manufacture theoretically from (9) types. From the result of an experiment,  $\text{CH}_4$  other than hydrogen of a some carries out a byproduction. This is considered to be generated by the reaction of  $\text{CO}_2$  and  $\text{H}_2$ . Since S minutes in coal are nonaqueous solubility although fixed as  $\text{CaSO}_4$  when not adding  $\text{Na}_2\text{CO}_3$ , the separation from other solid matter is difficult. However, by adding  $\text{Na}_2\text{CO}_3$ , finally S in coal is caught as water-soluble  $\text{Na}_2\text{SO}_4$ , and since it can extract out of a system by water treatment, it becomes advantageous.

[0013]

[Examples 5-8] Four kinds of coal system organic substance of the dry distillation object of the Australia YARUN charcoal (brown coal), the Pacific Ocean charcoal (bituminous coal), the Australia BUREA SOL charcoal (bituminous coal), and BUREA SOL charcoal in this sequence Make 0.1g into a sample, respectively and to this calcium ( $\text{OH})_2$  which is a carbon-dioxide absorbing material 0.6g, 0.1g of  $\text{Na}_2\text{CO}_3$  was mixed as a sulfur content scavenger which served water as the catalyst of four cc and a reaction, heat tracing was carried out with the electric furnace, and it was made to react on the reaction temperature of 650 degrees C, pressure 1000 atmospheric pressure, and the conditions for reaction-time 20 minutes. This example is considered that the same result is obtained also by the same pressure as the example shown in drawing 3 although pressures are 1000 atmospheric pressures and a high case. While cooling after the reaction, collecting the gas which occurred in the sampling bag and measuring generating capacity, the presentation was measured by the gas chromatograph. The solid-state and liquid inside a reactor analyzed by collecting. Drawing 4 shows an amount and a presentation of as opposed to 1g of carbon in a sample for the gas which occurred then. In addition, it is the amount of hydrogen in four sorts of coal system organic substance, and the Pacific Ocean charcoal which was shown in the middle in front Naka, and it is shown for a comparison of the amount of hydrogen when this is all emitted. Except for the dry distillation object of BUREA SOL charcoal, the hydrogen almost near the amount of theory was generated. Also to the dry distillation object of BUREA SOL charcoal, if reaction time is secured enough, the same result will be obtained. In the case of Pacific Ocean charcoal, it was shown, but since the amount of hydrogen generation which exceeds the amount of hydrogen generation calculated from the hydrogen content in the Pacific Ocean charcoal you to be Haruka is obtained, the hydrogen shown by drawing 4 is judged to be that by which the water supplied as a reaction raw material was converted into hydrogen by the reaction formula (2). Moreover, in generation gas, the matter which has the origin in the sulfur contained in coal is not detected, but sulfur is judged to be what was fixed as a solid-state or water-soluble matter.

[0014]

[Examples 9-12] a tree -- waste -- a polyvinyl chloride -- polyethylene -- black -- rubber -- four -- a kind -- the organic substance -- this -- sequence -- respectively -- 0.1 -- g -- a sample -- \*\* -- carrying out -- this -- a carbon dioxide -- an absorbing material -- it is -- calcium -- ( --  $\text{OH}$  -- ) -- two -- 0.6 -- g -- water -- four -- cc -- and -- a reaction -- a catalyst -- having served -- a sulfur content -- a scavenger -- \*\*\*\*\* --  $\text{Na}$  -- two --  $\text{CO}$  -- three -- 0.1 -- g -- mixing -- an electric furnace -- heat tracing -- carrying out -- reaction temperature -- 650 -- degree C -- a pressure -- 1000 -- an atmospheric pressure -- reaction time -- 20 -- a minute -- conditions -- reacting -- having made . While cooling after the reaction, collecting the gas which occurred in the sampling bag and measuring generating capacity, the presentation was measured by the gas chromatograph. The solid-state and liquid inside a reactor analyzed by collecting. Drawing 5 shows the amount of the gas which occurred then, and a presentation. Drawing 5 shows the experimental result at the time of applying this approach to the organic substance other than coal. He can understand that all the matter

containing the carbon content which can burn as the organic substance can be set as the object of this approach.

[0015]

[Application in the process of an example] The process shown in drawing 6 based on the result of examples 1-12 was possible. although many kinds of configurations are possible as a process -- this time -- as the basic plan of a process design -- (1) -- all required heat energy is provided with the coal which is a raw material.

(2) The heating method of a raw material adopts an internal heating method with high effectiveness. That is, coal slurry is heated using the heat of reaction of CaO.

It adopted. Under this concept, the conversion of C in injection coal will keep high a part for C in the solid rather picked out from a presser-foot reactor low, will decompose CaCO<sub>3</sub> and calcium (OH)<sub>2</sub> with the heat which converts C into CO<sub>2</sub> with air with a CaO regenerator (combustor of unburnt carbon) separately, and generates this in that case, and will reproduce them to CaO. In this case, CO<sub>2</sub> concentration in exhaust gas becomes about 25%. This is recoverable as the CaO regenerator, then CO<sub>2</sub> of about 100% of high concentration of a heat tracing method. This means that the carbon dioxides produced using coal can be collected by high concentration, and means that special concentration separation actuation is unnecessary. It becomes advantageous also from a viewpoint of greenhouse-gases discharge control. The material balance in the case of carrying out 1 t/hr processing of the coal from an experimental result and the heat balance were calculated. 50% of 1t of supplied coal reacts, and 1400Nm of the hydrogen and methane of 3 are generated. The carbon content which remained is burned with air or oxygen with a regenerator, and reproduces CaCO<sub>3</sub> and calcium (OH)<sub>2</sub> to CaO with the heat. Since the heat of the equivalent occurs in case CaO is mixed with H<sub>2</sub>O, most heat of combustion which coal finally has will be used for gas generation, and can attain high cold gas efficiency (ratio of the heat of combustion which the generated gas holds, and the heat of combustion which the supplied coal holds). When the heat needed with this regenerator is securable separately, generation capacity can be made to increase by gathering the conversion of a reactor.

[0016]

[Effect of the Invention] In this invention, it is characteristic for this approach to be able to be large also to the organic substance other than coal, and to be able to be adapted for it. The height of this flexibility also deserves attention. This process is roughly classified according to a raw material system as follows.

(1) In process process, the thing which use as a raw material process (4) biomass which uses as a raw material the process (3) plastics which use as a raw material the process (2) heavy oil which uses coal as a raw material, reduced pressure residual oil, etc. and for which a process is constructed to each raw material of a certain thing is possible for some difference, and it is efficient, and hydrogen is manufactured and it can prevent the discharge to the environment of a harmful element. Hydrogen can be thought by both sides of an energy recovery and matter recovery. Moreover, collecting by high concentration is also possible, CO<sub>2</sub> which carries out a byproduct is very advantageous also from a viewpoint of processing of CO<sub>2</sub> which is global warming gases, and use, and there is also little impact given to an environment. The technique which can be manufactured can be alternatively offered for hydrogen only in the combination of the heat-source matter of carbon content, such as coal, petroleum, biomass, and plastics, and cheap and common matter called water, air, a limestone, and a sodium carbonate. As concrete effectiveness, the load to an environment is not given but (1) fossil fuel resource (especially coal) and biomass can be changed into clean hydrogen energy. Various development of the approach of hydrogen being efficient as energy and using it is carried out, and, as a result, prolongation-of-life-ization of a fossil fuel resource can be performed.

(2) Even when moisture, such as brown coal, is included so much, it becomes possible to use as it is, without making it dry like the former.

(3) It is possible to catch the matter leading to environmental pollution, such as sulfur in the carbon content matter and chlorine, etc.

(4) plastics -- not a form but the hydrogen of heat energy -- conversion -- possible -- an energy recovery and matter recycle -- correspondence to both of the methods is possible.

There are no generating of dioxin and generating of a hydrogen chloride which pose a problem by incineration. \*\*\* is mentioned.

---

[Translation done.]

**\* NOTICES \***

**JPO and NCIPI are not responsible for any damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DESCRIPTION OF DRAWINGS**

---

**[Brief Description of the Drawings]**

**[Drawing 1]** The explanatory view having shown an example using the supercritical water by the conventional technique of the pyrolysis oxidation process of the organic substance

**[Drawing 2]** The sectional view of the equipment used for operation of this invention

**[Drawing 3]** The explanatory view showing the experimental result and the effectiveness of a catalyst of checking radical Motohara \*\* of this invention

**[Drawing 4]** The explanatory view showing the experimental result about the capacity generated at the reaction with the supercritical water of the various coal in the conditions of this invention, and its presentation

**[Drawing 5]** The explanatory view showing the experimental result about the capacity generated at the reaction with the supercritical water of the various organic substance other than \*\* and the coal in the conditions of this invention, and its presentation

**[Drawing 6]** The flow chart explanatory view having shown an example of the hydrogen manufacture process from the organic substance based on this invention

**[Description of Notations]**

1 -- Supercritical water reactor

2 -- Pump

3 -- Condensator

4 -- Gas eliminator

5 -- Micro autoclave

6 -- Reaction section

7 -- Capillary tube

---

**[Translation done.]**

